PHYLLOSILICATES, ZEOLITES, AND CARBONATE NEAR NILI FOSSAE, MARS: EVIDENCE FOR DISTINCT ENVIRONMENTS OF AQUEOUS ALTERATION.

B.L. Ehlmann[1], J.F. Mustard[1], G.A. Swayze[2], J.J. Wray[3], O.S. Barnouin-Jha[4], J.L. Bishop[5], D.J. Des Marais[6], F. Poulet[7], L.H. Roach[1], R.E. Milliken[8], R.N. Clark[2], S.L. Murchie[4], and the MRO CRISM Team. [1]Dept. of Geological Sciences, Brown University, [2]U.S. Geological Survey, Denver, [3]Cornell University, [4]JHU-Applied Physics Laboratory [5]SETI Institute [6]NASA Ames [7]IAS, Université Paris-Sud, [8]JPL-Caltech (bethany_ehlmann@brown.edu)

Introduction: The region west of the Isidis basin, near Nili Fossae, hosts the greatest mineral diversity mapped from orbit: olivine [1, 2], low- and high- calcium pyroxene [3], and iron-magnesium smectite [4-6]. High resolution targeted observations (18-36 m/pixel) from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [7] reveal diverse alteration minerals generated by aqueous processes, including nontronite, saponite, kaolinite, chlorite, illite or muscovite, carbonate, analcime and another zeolite, and a hydrated Si-OH bearing phase whose spectra are consistent with altered basaltic glass or opaline silica [4-6, 8-11]. The spatial distribution of these minerals (Fig. 1), suggests distinct mineralogic provinces which may indicate different environments for aqueous alteration or different starting materials. Both near surface and subsurface—possibly hydrothermal—settings of neutral to alkaline pH are implicated by the mineralogy and geomorphology of the provinces discussed below.

"Provinces" of alteration: Three distinct provinces of alteration mineral assemblages are tentatively identified:

(1) *Western*: Near the Antoniadi basin, multiple generations of impact craters are superposed on one another. Fe/Mg smectite, chlorite and hydrated Si-OH bearing phases are found, usually associated with crater central peaks and walls. The zeolite analcime is detected in the central peaks of two craters (e.g. Fig. 2A; [10]) that also exhibit "quartzofeldspathic" (QF) material [12]. Chlorite, smectite, and zeolite occur in small knobs within the central peak, while the Si-OH phase is associated with aeolian deposits at the base of the peak which also hosts the QF material.

(2) *Central*: West of Nili Fossae near a 50 km crater, chlorite is the dominant phyllosilicate with Fe/Mg smectite and a mica, illite or muscovite, as minor phases [9]. The strongest mineral signatures are associated with small craters and topographic highs. At the base of some of these highs, areas polygonally fractured at meter-scale contain chlorite (Fig. 2B). Elevation around the crater is asymmetric with the chlorite/mica-rich eastern side lower by several hundred meters. This may reflect pre-impact topography or may indicate chlorite and illite are exposed by erosion from the lower portion of the ejecta blanket or underlying crust.

(3) *Eastern*: This region encompasses the concentric grabens of Nili Fossae which formed between the inner and outer rings of the basin during structural readjustment following the Isidis impact ~3.9 Ga [13]. West and south of Isidis in Nili Fossae and Libya Montes, a consistent stratigraphy is observed with a basement of Fe/Mg smectites and low-calcium pyroxene overlain unconformably by olivine and a mafic cap rock [5].

While the regional Fe/Mg smectite-bearing rocks are cut by the fossae, placing their age as early Noachian [4, 6, 13], there is geomorphic evidence for the continued presence of water into the Hesperian from valleys and channels which dissect both the Noachian cratered terrains and the Hesperian Syrtis Major lavas. Filled craters, alluvial fans, and a 15,000 km^2 valley system feeding Jezero crater lake provide evidence for extensive sedimentary transport [6, 14-15].

Kaolinite is found in 11 locations and typically occurs as the topmost layer of phyllosilicate, found in a tens of meters thick layer above Fe/Mg smectite (Fig. 2C). It is sometimes the uppermost unit and sometimes exposed from beneath apparently unaltered mafic cap rock. Eastern Nili Fossae also hosts a phase most likely to be carbonate, specifically magnesite [8]. With the exception of carbonate associated with transported sediments within Jezero crater, the carbonate is in a rock unit above and draped over

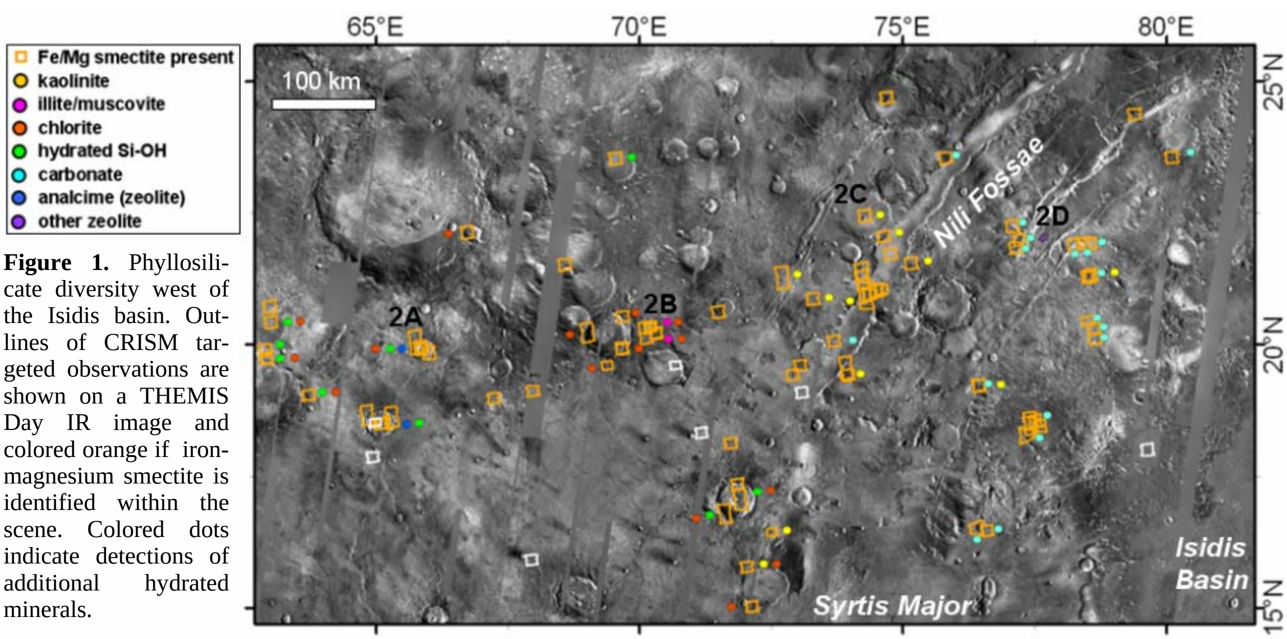

Figure 1. Phyllosilicate diversity west of the Isidis basin. Outlines of CRISM targeted observations are shown on a THEMIS Day IR image and colored orange if iron-magnesium smectite is identified within the scene. Colored dots indicate detections of additional hydrated minerals.

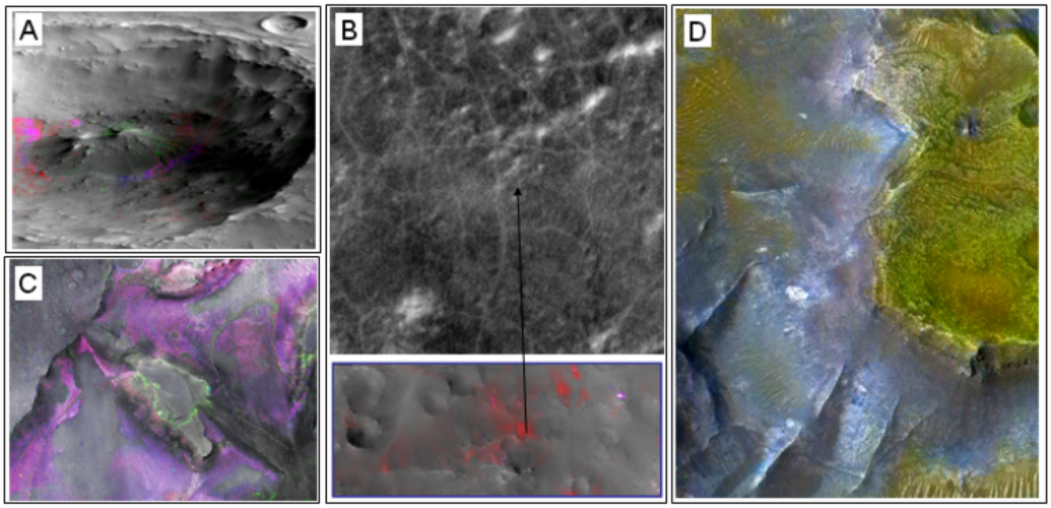

Figure 2. (A) Fe/Mg smectite and chlorite (green) along with zeolite (red) in the ~4 km wide crater central peak, which is surrounded by hydrated silica-bearing aeolian sediments (magenta-blue) (B) fractured chlorite-bearing terrain (polygons are ~10-20m). Chrolite (red) and illite (magneta) are associated with topographic highs near 500m craters (C) a kaolinite layer (green), exposed in a 2 km wide mesa, caps a thick Fe/Mg smectite basement (magneta) (D) Olivine (yellow) and carbonate (green) overlie Fe/Mg smectite (blue). Image is 1km across.

Fe/Mg smectites and beneath a mafic cap rock, in a similar stratgraphic position to olivine (Fig. 2D). The carbonate is light toned and layered with extensive polygonal fracture patterns. It and the mafic cap are both cut by valleys, indicating formation was likely subsequent or coincident with valley formation (no later than Hesperian).

Implications: Distinct assemblages of minerals suggest that the nature of aqueous activity varied in space and time across the region west of the Isidis basin. Fe/Mg smectites are exposed as the lowermost unit in images sampling over 100,000 km^2. The great spatial extent of this unit seems to exclude lacustrine or volcanic hydrothermal processes as the primary mechanism for regional smectite formation and instead favors pervasive near surface alteration or hydrothermal/metamorphic alteration in the crust [16]. However, existence of multiple secondary minerals suggests locally more intensive or distinct processes for alteration.

Eastern Nili Fossae crustal materials apparently experienced multiple episodes of aqueous activity. The first was early Noachian alteration, which formed a Fe/Mg smectite-rich basement. Later episode(s) are indicated by fluvial geomorphology and by mineralogic evidence, namely kaolinite and carbonate. A plausible formation mechanism for a capping kaolinite layer on smectite deposits is top down leaching of pre-existing phyllosilicates, leading to loss of Ca, Mg, and Fe ions from smectite and its transformation to kaolinite.

Carbonate formation conditions are more ambiguous and may have taken place in the surface or subsurface. The carbonate may have formed in the same episode as the kaolinite, by alteration of olivine by water at the surface and subsequent emplacement of mafic cap rock. An alternative is carbonate formation at depth by a initiation of metasomatic alteration along a contact between hot olivine bearing rocks and underlying hydrous Fe/Mg smectite. A key control on carbonate distribution appears to be existence of precursor ultramafic rock, since carbonate is not observed moving west as olivine abundance decreases. In any case, the persistence of carbonate to the present indicates waters interacting with this unit were not acidic.

Greater mineral diversity in the Central and Western provinces may have been generated in local hydrothermal systems related to impact events. The mineralogy associated with impact craters in the Central and Western provinces is remarkably similar to the Fe/Mg-rich smectites or chlorites with accessory zeolite, silica, quartz, and K-feldspar which result from hydrothermal alteration in terrestrial craters [17]. Such an assemblage suggests the QF material [12] may be hydrothermal rather than igneous. The low TES-modeled abundances of quartz and K-spar and association with hydrated Si-OH bearing phases (e.g. altered impact glass [11]) are consistent with such a formation process. Experimental data show smectite-zeolite assemblages result from glasses and or basalt powders and are stable at temperatures <150°C [18] while illite-chlorite assemblages are stable at T>200°C [17]. Hence, variation in the temperature of the hydrothermal system may result in the distinctive Central and Western assemblages.

An alternative hypothesis is that alteration materials associated with craters reflect changes in underlying crustal materials westward of the Isidis basin and that aqueous alteration pre-dated formation of the impact structures in which these minerals are mapped. Smectite transforms to illite upon burial at T>50-80°C [19]. Illite and chlorite altered at depth may have been excavated by impact.

Collectively, the data indicate multiple episodes of aqueous activity, perhaps resulting from multiple processes, and suggest that the region west of the Isidis basin was over early Mars history persistently and unusually water-rich.

Acknowledgements: Thanks to the ongoing efforts of the MRO operations team, and the HiRISE and CTX teams for coordinating with CRISM, enabling high resolution studies combining geomorphology and mineralogy.

References: [1] Hoefen, T.M. et al. (2003) *Science*, 302, 627-630 [2] Hamilton, V.E., Christensen P.R. (2005) *Geology, 33*, 433-436 [3] Mustard J.F. et al. (2005) *Science, 307*, 1594-1597 [4] Poulet F. et al. (2005) *Nature, 438*, 623-627 [5] Mustard, J.F. et al. (2008) *Nature 454, 305-309* [6] Mangold, N. et al., *JGR* 112, E08S04 [7] Murchie, S.L. et al. (2007) *JGR* 112, E05S03.[8] Ehlmann, B.L. et al., submitted, *Science.* [9] Ehlmann, B.L. et al. 2007, *7th Mars Conf*., Abs. #3270 [10] Ehlmann, B.L et al., (2008) *LPSC 39*, Abs. #2326. [11] Swayze, G.A. et al., 2007, *7th Mars Conf.* Abs. #3384 [12] Bandfield, J.L. (2006) *GRL* 33, L06203. [13] Mustard, J.F. et al., (2007) *JGR* 112, E08S03 [14] Ehlmann, B.L. et al. (2008) *Nature Geosci*. 1, 355-358 [15] Fassett, C.I. and Head, J.W. (2005) *GRL* 32, L14201. [16] Parmentier, E.M. (2008) LPSC 39, Abs. # 1544 [17] Allen, C.C. et al. (1982) *JGR* 87, 10,083-10,101. [18] Robert, C. and Goffe, B. (1993), *Geochim. Cosmochim. Acta* 57, 3597-3612. [19] Hower, J. (1981) *Clays & Resource Geol.* Min. Assoc. Can., 60-80.